

# Martensitic stainless steels in context

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**Abstract**

This paper explains the overall growth of the CRA flowline market and describes how weldable martensitic stainless steels developed as materials for flowlines carrying corrosive oil and gas production fluids.

## Why choose CRAs for Flowlines?

Early oil production used entirely carbon steel production facilities including carbon steel flowlines. This was very successful, because the oil tends to form a protective film over the surface of steel thus inhibiting corrosion. In very general terms, oil wells tend not to be highly corrosive, at least in their early days. As time passes, oil wells tend to produce increasing amounts of water and gradually this protective oil film on the surface becomes less effective and oil wells with high water cuts can be rather corrosive.

By contrast, gas wells do not have the same benefit of a protective oil film. As the gas is produced from the wells it is gradually cooling down from the bottom well temperature to the surface temperature. This cooling is accompanied by condensation of water from vapour in the gas. The condensed water contains dissolved acid gases, CO<sub>2</sub> and H<sub>2</sub>S. The resulting pH of the condensed water is typically between 3.5 and 4.2 and corrosion rates of plain carbon steel can be very high, sometimes several mm per year.

It is quite common practice to control this corrosion through the use of chemical inhibitor additions to the well fluids. However there are some practical problems and some economic issues in doing so. In some projects:

- The well design is unsuitable for injecting inhibitor.
- The corrosion rate is too high, even with inhibitor injection.
- The cumulative cost of purchasing inhibitor year on year can become excessive.
- High reliability is required in the inhibitor injection system which cannot always be guaranteed.
- The environmental disposal issues with inhibitors are too

demanding.

In such cases the normal choice of material for the flowlines would be a corrosion resistant alloy (CRA). CRA pipelines have proven to have higher reliability than carbon steel with inhibition. CRA pipelines often have lower life cycle cost (references 1 to 6) and much less environmental impact (reference 7).

The use of CRA flowlines dates back to 1975. Their application is almost entirely the story about the development of gas as a fuel.

This paper discusses which types of CRAs have been selected over the past 30 years and discusses trends in selection.

## Pioneers in CRA Flowlines!

Considering the first applications of CRA flowlines in the period 1975-1980, the Dutch operating company, NAM, was the main pioneer. In this period, 7 flowlines internally clad with stainless steel AISI 316L (total length 7.7km) and four duplex stainless steel lines (total length 13.3km) were installed, two of the duplex lines being the first offshore CRA flowlines.

NAM was becoming a major producer of gas but was familiar with the corrosion problems caused by the CO<sub>2</sub> which was produced with the methane. Whilst standard austenitic stainless steels such as AISI 304L or 316L were immune to the corrosion, they were unsuitable for the high pressure application of flowlines because of their low yield strength (typically 180MPa minimum). However, using the austenitic stainless steel as a cladding on a much stronger backing steel (X52 in the first flowlines of yield strength 360MPa) allowed the wall thickness

to be reduced by about 50% compared to a solid austenitic stainless steel. This had many practical benefits in reducing weight and welding time, but also in lower material cost.

Similarly the duplex stainless steel 3RE60 was already used for some facilities piping because of its resistance to CO<sub>2</sub> corrosion. Because of the high yield strength of duplex stainless steel (typically 450MPa) the wall thickness of the pipe was greatly reduced compared to an austenitic grade, making it economically feasible to select these grades.

The first two duplex lines were made from alloy 3RE60 (18%Cr), but this was quickly superseded by the DIN 1.4462 duplex stainless steel. This has 22%Cr and is now known internationally as UNS S31803 – the workhorse duplex stainless steel for the majority of subsequent duplex flowlines. A tighter specification, UNS 32205 has also been used. Both grades are included under the designation 22%Cr in this paper.

## The Duplex Story

By the end of 1990 there were over 238km of duplex stainless steel (DSS) pipelines installed in 34 projects. Many of these were in the Netherlands, but several were distributed throughout the developing North Sea, both in the UK and Norwegian sectors and some in the USA (McElmo Dome) and Canada.

1990 was a significant year for duplex stainless steel in flowlines as it saw the first application of the higher grade material, 25%Cr “Superduplex”. This grade offered even greater corrosion resistance (for instance to some level of H<sub>2</sub>S) and also even higher yield strength (550MPa).

The growth in use of duplex stainless

steel in this decade was phenomenal, with more than 1136km installed by the year 2000. Of this quantity, 91.1% is 22%Cr, 8.6% is 25%Cr and 0.3% 3RE60.

Figure 1 shows the length of DSS pipelines installed to date of varying nominal diameters. 59% of installed pipe is less than or equal to 8 inch in diameter which is typical of individual flowlines from single wells.

## The Clad Story

Clad pipe grew steadily over a 20 year period in parallel with the application of duplex stainless steels. In many cases clad pipe would be regarded as a direct technical alternative to duplex stainless steel. The choice of AISI 316L stainless steel as a cladding material is very suitable for overcoming corrosion due to CO<sub>2</sub>. The choice of AISI 316L cladding or solid DSS would generally be made on economic grounds.

However, conditions in the oil and gas industry do not stay constant for very long and as time has progressed it has become necessary to exploit increasingly corrosive reservoirs to meet the continuous demand for gas production. Some of the production conditions being encountered towards the end of the 1980s would have been considered too corrosive for either AISI 316L clad pipe or for duplex stainless steels because of the increasing levels of hydrogen sulphide in the gas stream making the environment "sour".

The great versatility of clad pipe in being able to change just the cladding layer which is in contact with the gas for another alloy more suited to the conditions is one of the great attractions of this material choice. From 1986 onwards there is increasing use of nickel Alloy 825 clad pipe, which is the normal material selected for handling sour conditions. By 1991 the amount of Alloy 825 clad pipe installed exceeded the amount of AISI 316L clad pipe (Figure 2). Occasionally other alloys such as C276 and AISI 904L have been selected for particular conditions.

Figure 3 shows the length of clad pipelines installed as a function of the nominal diameter. Approximately 67% of the clad pipe installed is greater than 8inch in diameter reflecting its wide use for gathering pipelines, handling production from a manifold

of several wells.

Figures 4 and 5 illustrate the range of choice of cladding alloy and backing steel for all projects to date. Current alloy choices tend to be AISI 316L for non-sour conditions and Alloy 825 for sour conditions. The backing steel most frequently selected is grade X65.

Figure 6 illustrates the range of production methods for clad pipe showing that 48.2% of the installed pipe has been made by hydraulically gripping (lined pipe), 40.7% by longitudinally welding clad plate and a small but growing amount (1.8%) made by weld overlaying the inside of a carbon steel billet with an alloy and then extruding it to make seamless clad pipe.

## The Martensitic Stainless Steels Story

The very first application of martensitic stainless steel (MSS) for pipelines was by Mobil in the Arun field in Indonesia. More than 28 km of standard 13 Cr martensitic stainless steel was installed over a period of 13 years from 1981.

It was the emergence in 1996 of the newly developed low carbon weldable grades of alloyed 13 Cr martensitic stainless steel which changed the CRA flowline use significantly. Already used for many years for downhole tubing this "Super 13Cr" was a material with a strong track record as an economical choice for combating CO<sub>2</sub> corrosion and mildly sour conditions.

Relative to other CRA Flowline Material choices, Super 13 Cr is less expensive. Not only is it somewhat lower in Alloy content than duplex stainless steels, but it can be produced in bulk on some of the world's largest steel pipe production lines which have much greater productivity than most stainless steel pipe producers internationally. Thus, this material was not only established from a corrosion viewpoint, but it was also a very economic flowline material choice. Not surprisingly application of this material has been substantial with approximately 650 km installed between 1996 and 2002!

The majority, 91.3%, has been seamless; the rest split between centricast pipe (4.4%) used principally

in the Arun field and longitudinally welded pipe (4.3%) produced by laser or other welding processes.

Figure 7 shows the length of MSS pipelines installed as a function of the nominal diameter. Only 1% of the installed pipelines are greater than 16 inch in diameter, 60% being between 8 and 14 inch. The majority of these pipelines are connecting manifolds (mostly subsea) with several wellheads to production platforms.

## General Trends

The total market for CRA flowlines has increased over the past 25 years because of increasing demands for gas (e.g. for direct supply to coastal power stations), the trend towards smaller field developments tying into existing infrastructure and the trend for new fields to be in increasingly corrosive and therefore requiring greater use of CRAs in general.

Considering the overall CRA flowline market, Figure 8 shows the length of different types of CRA flowlines installed per year. The peak levels of activity in 1996-1997 coincide with major development of Norwegian Gas fields, which used MSS for the flowlines and gathering lines to handle their mostly sweet conditions. This was combined with numerous duplex stainless steel pipelines being installed in the UK sector of the North Sea and in Korea and a large clad line in the UK North Sea.

Figure 9 illustrates the "share" of each type of CRA material over 5 year periods showing the substantial rise in the selection of MSS following the emergence of the Super 13Cr grade for welded applications in the mid 1990's. The period 2000-2002 is only a 3 year period and there are other projects ongoing which are known to require clad and possibly DSS flowlines so the share of MSS is estimated to be about 40% over the full 2000-2004 period.

On a cumulative basis Figure 10 shows the steady rise in installations of CRA flowlines since 1975 with the majority being DSS but a recent high rise in MSS. The total % use of different CRAs to date is shown in Figure 11.

Data on exact individual flowline lengths is not always known as suppliers tend to report "total" length of pipe supplied per project. However, evaluation of the data, for example of clad pipeline supplies, shows that the maximum length of flowlines has

been generally increasing with individual flowlines of around 30km becoming quite common. Also the average flowline length has been increasing (based on 4 year moving average) from about 1km in the 1970's and 1980's to about 6km in the 1990's (Figure 12). These trends to longer flowline lengths are typical of all CRA materials and reflect the tendency to tie in new developments to existing infrastructure. Such tie-ins, even with quite long CRA pipelines can be much more economic than the installation of a new processing platform as required to handle corrosive produced fluids in carbon steel equipment.

Considering the trends indicated in Figures 8, 10 and 12 it is anticipated that the future markets for CRA flowlines will tend to grow from the current level of approximately 120-150km/year. This is expected as more and more developments are being made which require tie-ins to existing facilities at greater distance. Furthermore the general trend to developments which are in inaccessible places (deep water or remote parts of the world which are difficult to support with operational staff) will encourage the selection of CRA materials for flowlines and gathering lines.

The future shift towards more corrosive production conditions, particularly more sour developments, will encourage the demand for pipelines clad with materials like Alloy 825 and Alloy 625.

Still, overall the gas industry will favour the least expensive option for materials and so the market for MSS is expected to remain steady at about 40% of the total CRA market when considered over the longer term despite short term variations in demand.

## Conclusions

Since 1975 a total of about 2400km of CRA flowlines have been installed of which 49% is duplex stainless steel, 23% clad carbon steel and 28% martensitic stainless steel.

During the longer term it is expected that the proportion of martensitic stainless steel will increase to around 40%, as a relatively inexpensive choice of CRA for the less corrosive

conditions.

About 27% of the flowlines installed are expected to be duplex stainless steels which have a greater range of application in terms of corrosion resistance than the martensitic stainless steels.

Pipelines clad with nickel alloys will tend to be selected for the more corrosive and sour conditions, increasing to about 33% of the future total CRA market.

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Fig. 1 - Nominal OD, inches, of installed DSS pipes, km

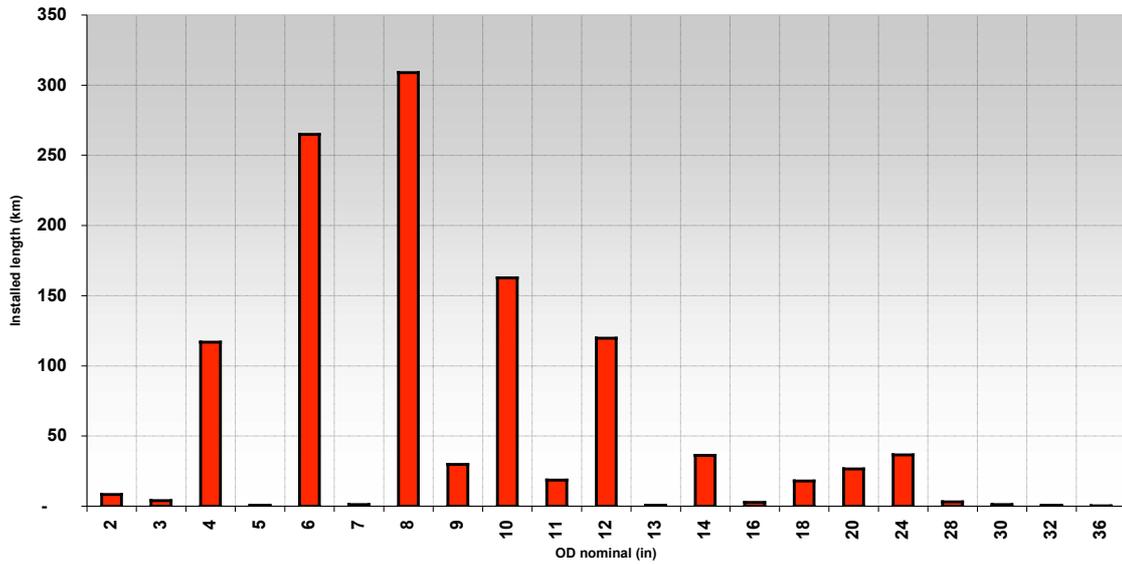


Fig. 2 - Cumulative selection of alloys for clad pipe, km

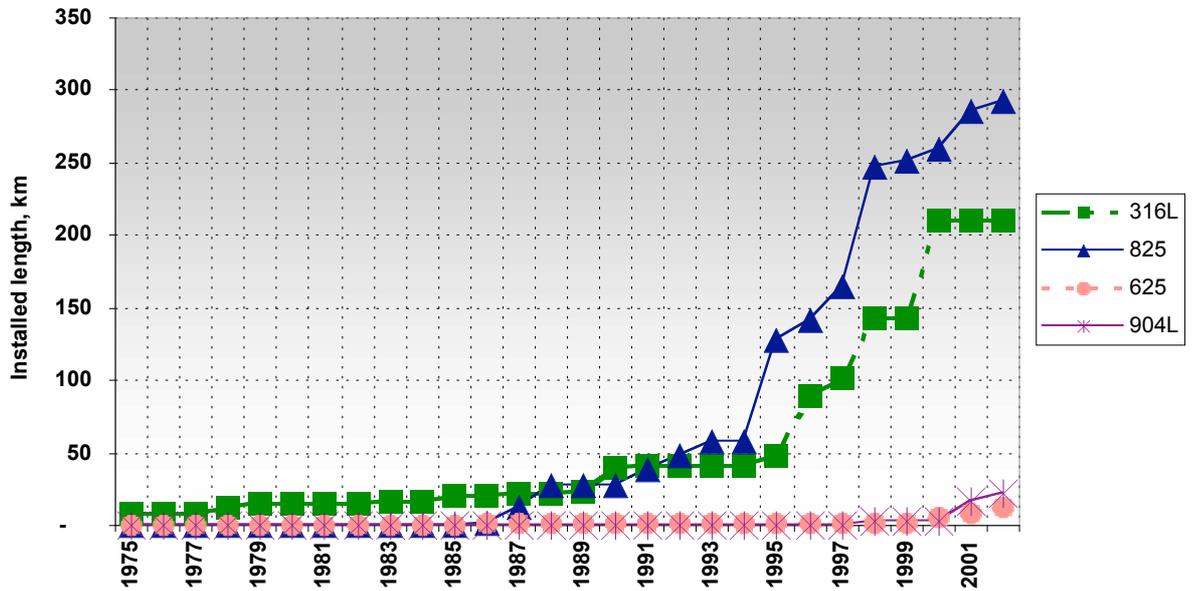


Fig. 3 - Nominal OD, inches, of installed clad pipes, km

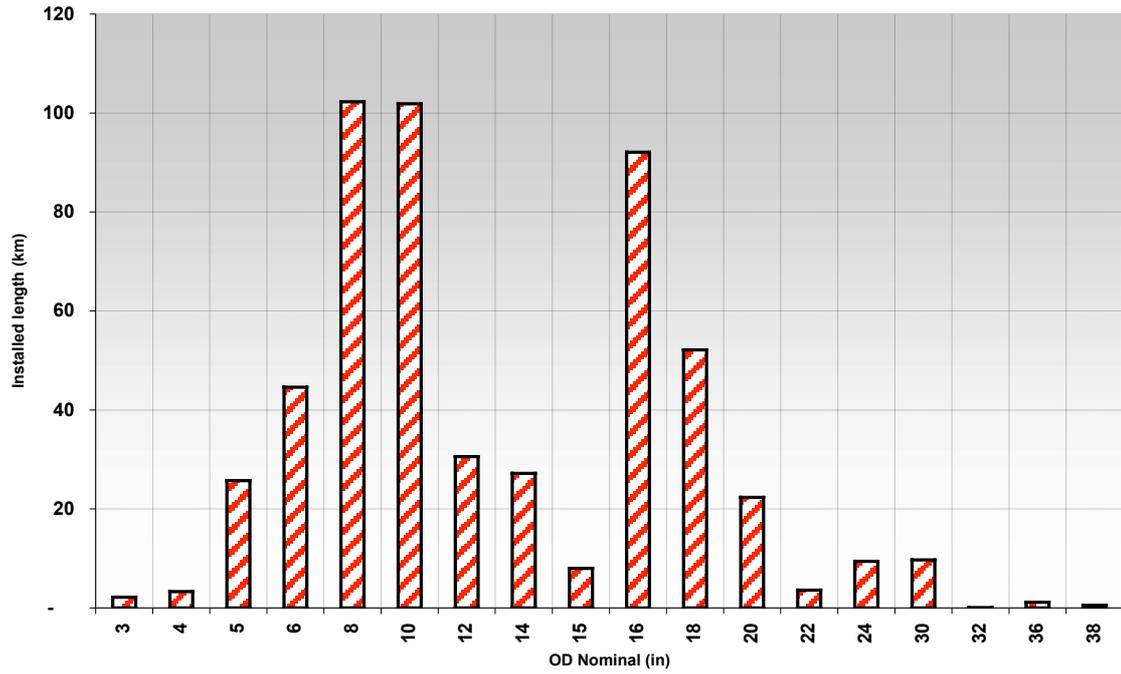


Fig. 4 - Selected cladding alloy of clad pipes installed to date by length

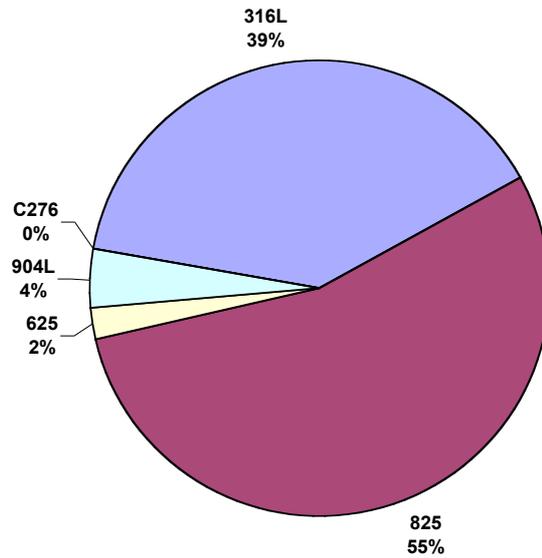


Fig. 5 - Backing steel of clad pipes installed to date by length

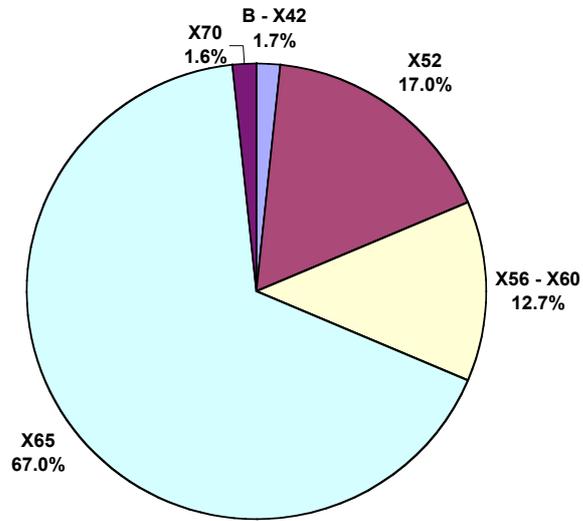


Fig. 6 - Manufacturing process of clad pipes installed to date by length

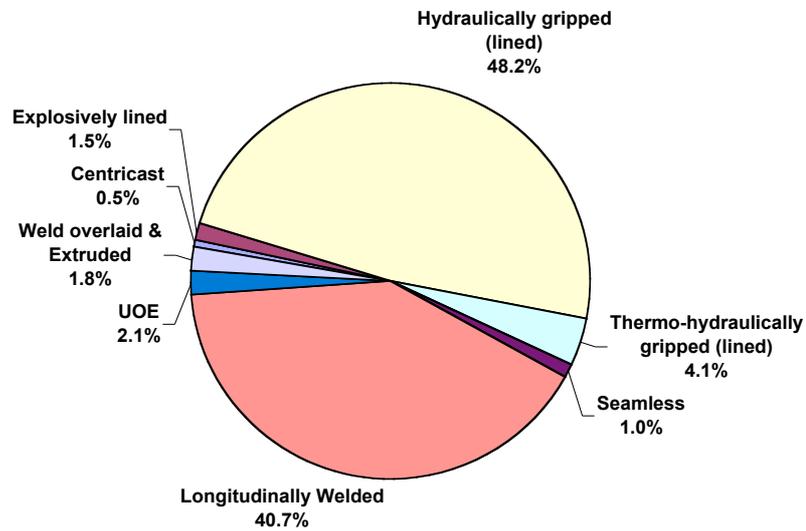


Fig. 7 - Nominal OD, inches, of installed MSS pipes, km

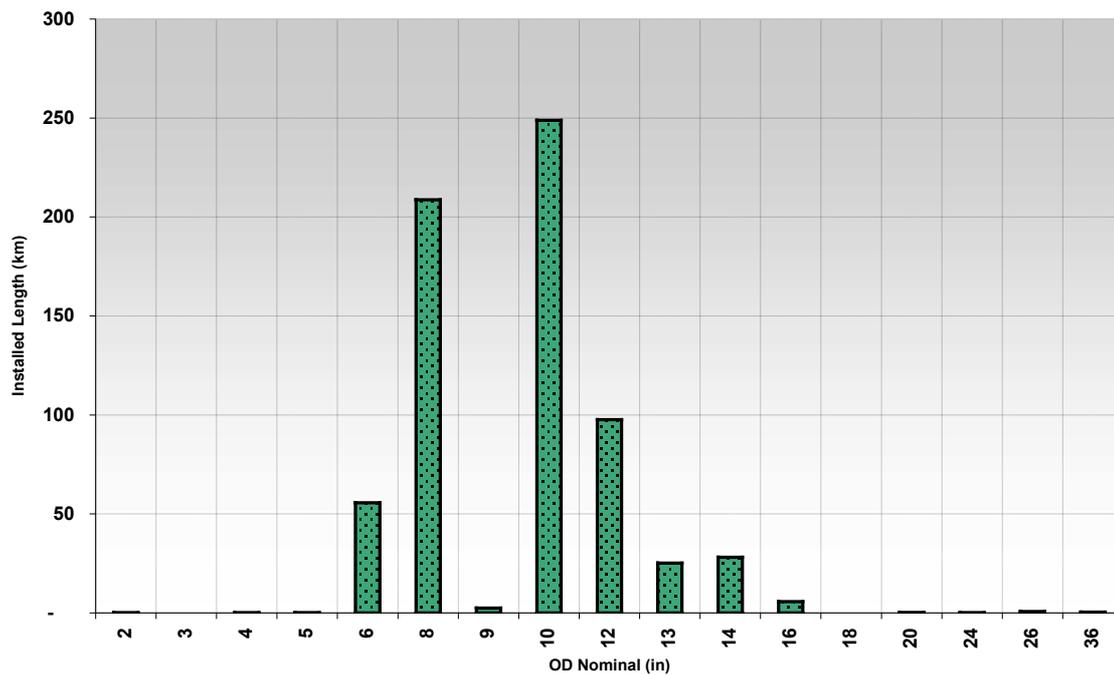
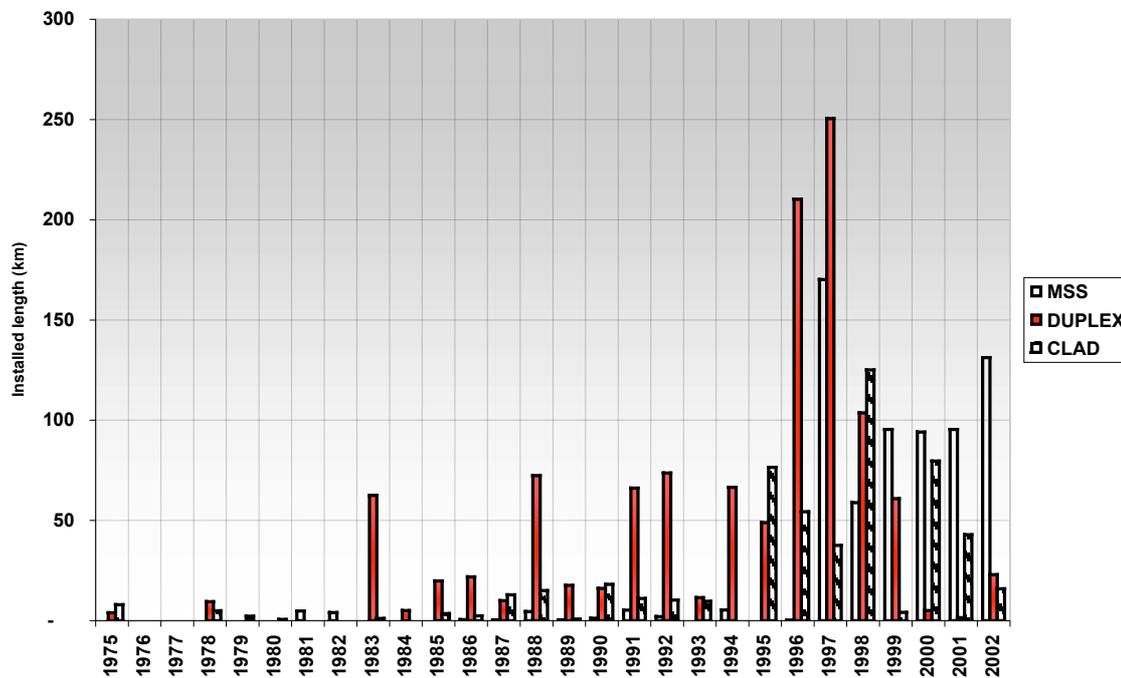


Fig. 8 - Quantity of CRA Pipes installed per year



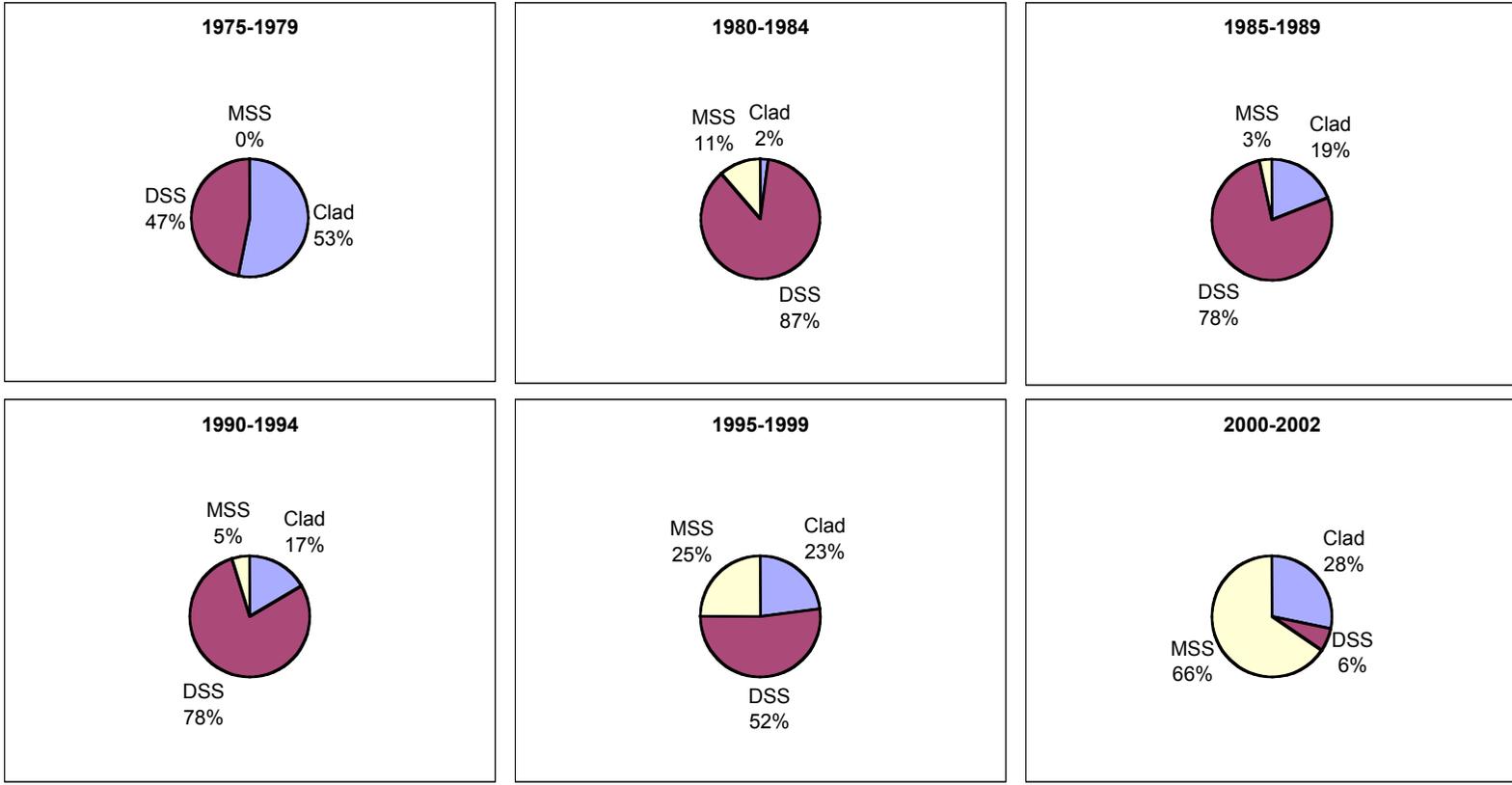


Fig. 9 - % share of different types of CRA flowline (km) in 5 yearly periods

Fig. 10 - Cumulative Use (km) of CRA Pipes

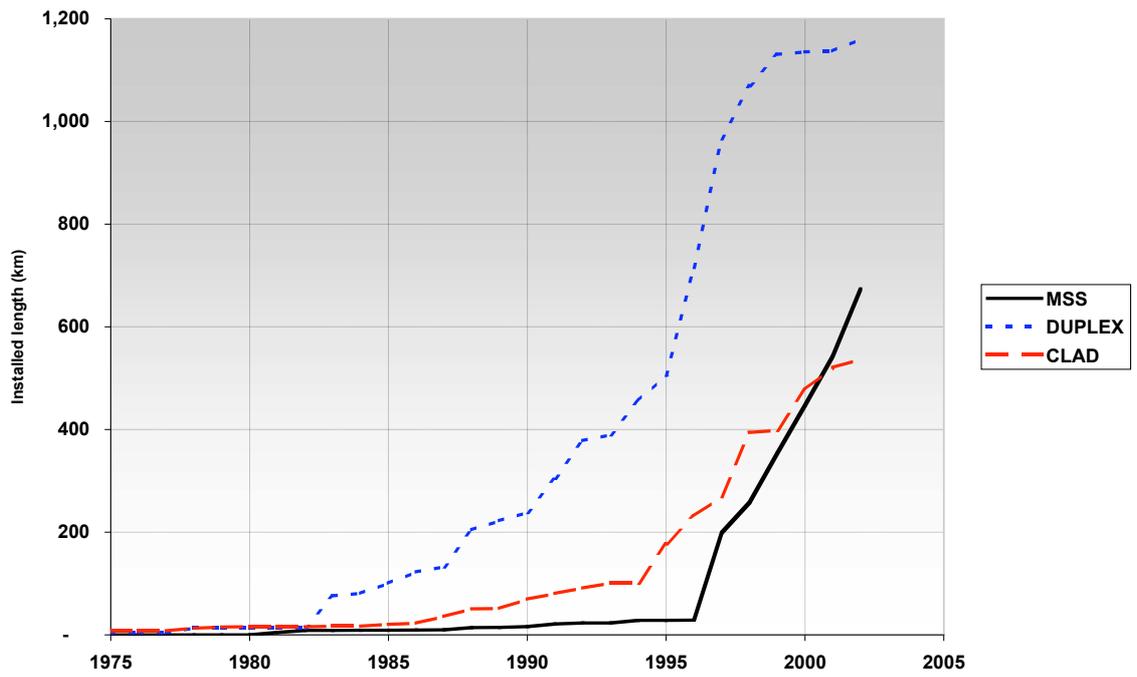


Fig. 11 - Total use of CRA (by length) to now

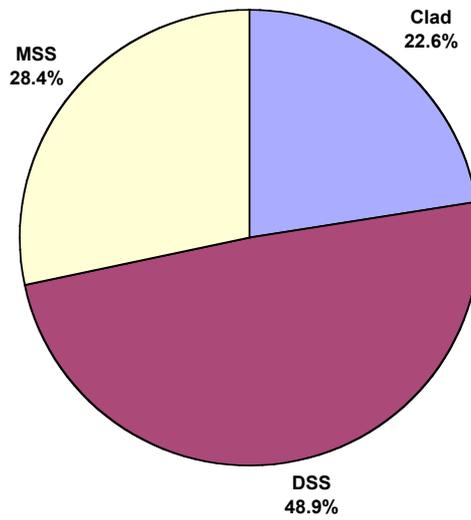


Fig. 12 - Max. length of individual clad flowline installed in a year and moving average of all clad lines installed over 4 year period

